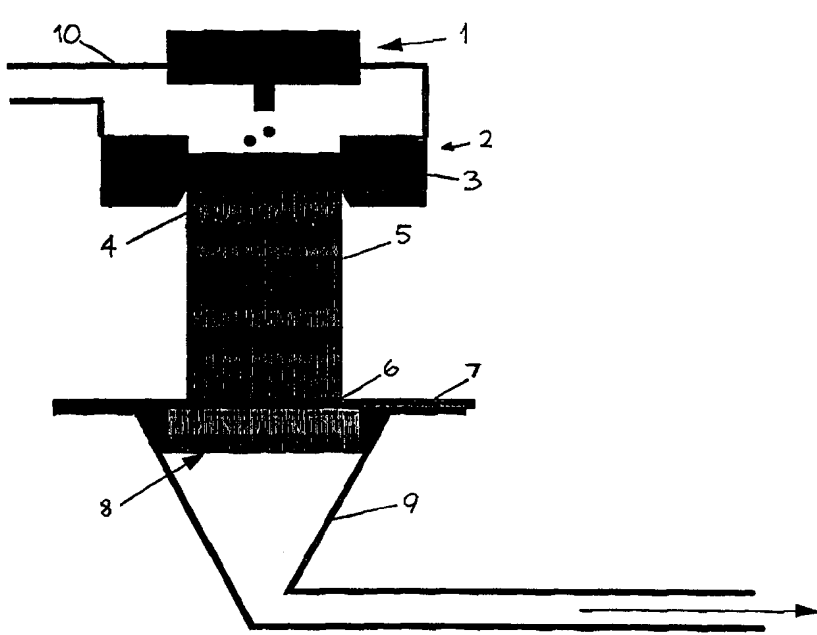




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B01J 37/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/47260</b> <b>(43) International Publication Date:</b> 23 September 1999 (23.09.99)
<b>(21) International Application Number:</b> PCT/GB99/00652 <b>(22) International Filing Date:</b> 5 March 1999 (05.03.99)  <b>(30) Priority Data:</b> 9805815.9      19 March 1998 (19.03.98)      GB  <b>(71) Applicant (for all designated States except US):</b> JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ADERHOLD, Dirk [DE/GB]; 17 Kingston Vale, Royston, Herts SG8 9UG (GB). HAYNES, Alan, George [GB/GB]; 1 Park Terrace, North End, Bassingbourn, Royston, Herts SG8 5NY (GB). SPENCER, Michael, Leonard, William [GB/GB]; 4 Jeve Close, Baldock, Herts SG7 6TP (GB). WINTERBOURN, Duncan, John, William [GB/GB]; 13 Faulkner Close, Milton, Cambridge CB4 6EF (GB).  <b>(74) Agent:</b> WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		<b>(81) Designated States:</b> AU, CA, JP, KR, MX, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> MONOLITH COATING APPARATUS AND METHOD THEREFOR   <b>(57) Abstract</b> <p>Apparatus for coating a support such as a monolithic catalyst support (5) comprises a dispenser (1) for dispensing a predetermined quantity of coating liquid, a containment (2) for the liquid and a source of vacuum (8, 9) which can be actuated to draw the entire quantity of coating liquid into the support (5). The apparatus and method are particularly useful for coating car catalysts without wastage and with increased design options.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<b>AL</b>	Albania	<b>ES</b>	Spain	<b>LS</b>	Lesotho	<b>SI</b>	Slovenia
<b>AM</b>	Armenia	<b>FI</b>	Finland	<b>LT</b>	Lithuania	<b>SK</b>	Slovakia
<b>AT</b>	Austria	<b>FR</b>	France	<b>LU</b>	Luxembourg	<b>SN</b>	Senegal
<b>AU</b>	Australia	<b>GA</b>	Gabon	<b>LV</b>	Latvia	<b>SZ</b>	Swaziland
<b>AZ</b>	Azerbaijan	<b>GB</b>	United Kingdom	<b>MC</b>	Monaco	<b>TD</b>	Chad
<b>BA</b>	Bosnia and Herzegovina	<b>GE</b>	Georgia	<b>MD</b>	Republic of Moldova	<b>TG</b>	Togo
<b>BB</b>	Barbados	<b>GH</b>	Ghana	<b>MG</b>	Madagascar	<b>TJ</b>	Tajikistan
<b>BE</b>	Belgium	<b>GN</b>	Guinea	<b>MK</b>	The former Yugoslav Republic of Macedonia	<b>TM</b>	Turkmenistan
<b>BF</b>	Burkina Faso	<b>GR</b>	Greece	<b>ML</b>	Mali	<b>TR</b>	Turkey
<b>BG</b>	Bulgaria	<b>HU</b>	Hungary	<b>MN</b>	Mongolia	<b>TT</b>	Trinidad and Tobago
<b>BJ</b>	Benin	<b>IE</b>	Ireland	<b>MR</b>	Mauritania	<b>UA</b>	Ukraine
<b>BR</b>	Brazil	<b>IL</b>	Israel	<b>MW</b>	Malawi	<b>UG</b>	Uganda
<b>BY</b>	Belarus	<b>IS</b>	Iceland	<b>MX</b>	Mexico	<b>US</b>	United States of America
<b>CA</b>	Canada	<b>IT</b>	Italy	<b>NE</b>	Niger	<b>UZ</b>	Uzbekistan
<b>CF</b>	Central African Republic	<b>JP</b>	Japan	<b>NL</b>	Netherlands	<b>VN</b>	Viet Nam
<b>CG</b>	Congo	<b>KE</b>	Kenya	<b>NO</b>	Norway	<b>YU</b>	Yugoslavia
<b>CH</b>	Switzerland	<b>KG</b>	Kyrgyzstan	<b>NZ</b>	New Zealand	<b>ZW</b>	Zimbabwe
<b>CI</b>	Côte d'Ivoire	<b>KP</b>	Democratic People's Republic of Korea	<b>PL</b>	Poland		
<b>CM</b>	Cameroon	<b>KR</b>	Republic of Korea	<b>PT</b>	Portugal		
<b>CN</b>	China	<b>KZ</b>	Kazakistan	<b>RO</b>	Romania		
<b>CU</b>	Cuba	<b>LC</b>	Saint Lucia	<b>RU</b>	Russian Federation		
<b>CZ</b>	Czech Republic	<b>LI</b>	Liechtenstein	<b>SD</b>	Sudan		
<b>DE</b>	Germany	<b>LK</b>	Sri Lanka	<b>SE</b>	Sweden		
<b>DK</b>	Denmark	<b>LR</b>	Liberia	<b>SG</b>	Singapore		
<b>EE</b>	Estonia						

## MONOLITH COATING APPARATUS AND METHOD THEREFOR

The present invention concerns improvements in a manufacturing process, and more especially concerns apparatus and methods suitable for the manufacture of catalysts supported on monolithic supports and like products.

5           Large numbers of catalysts supported on high surface area monolithic supports are manufactured each year. One of the principal types of such catalyst is the catalytic convertor for the internal combustion engine, and the present invention has particular utility in relation to these. For conciseness, the following description will particularly describe the use of the invention for car catalysts, but it should be understood that the invention may find  
10 application in all similar types of catalyst, whether for vehicles ("car catalysts" is intended to include trucks, utility vehicles, buses, motorcycles *etc*), ships, stationary power sources or gas clean-up from other industrial processes. The present invention is also useful in the manufacturing of like products where a coating is applied to a carrier, and we mention particularly absorber/desorber coatings, many of which are used in exhaust emission control.  
15 Such products are not technically "catalysts". We would mention particularly NO<sub>x</sub> absorbers, hydrocarbon absorbers, absorbers for sulphur compounds, and water vapour absorbers. As well as absorbers for gas treatment, absorbers may find use in heat pumps, *eg* air conditioning coolers.

20           The car catalyst is generally supported on an extruded ceramic, *eg* cordierite, or manufactured metal through-flow honeycomb substrate. The substrates are generally cylindrical, but may be oval or "racetrack" or a skewed oval, and have an effective continuous outer skin. (If the support or substrate does not have a continuous skin, the present invention may be used if the support or substrate is located within a sleeve.) Such  
25 substrates are very well known and are commercially available, and may have from 50 to 1200 cells/sq in. In order to increase the surface area for catalysis, it is commonplace to coat the substrate with a washcoat, comprising a slurry of high surface area particles such as alumina, optionally containing other components such as soluble and/or supported catalytically active platinum group metals ("PGMs"), promoters such as ceria, zirconia,  
30 barium *etc* and other components or absorptive materials such as silica, zeolite *etc*. In some

cases, after the washcoat is applied and dried and/or fired to give an adherent coating, one or more catalyst layers is applied. This may be by impregnation of solutions of one or more PGMs, generally selected from one or more of platinum, palladium and rhodium, and/or soluble promoters and/or by applying more layers of the same or different types of catalytically active or absorptive washcoats. The coating processes in use are usually considered as confidential know-how, but are generally variations on immersing the substrate in the slurry or solution, or passing the substrates through a curtain or waterfall of the slurry or solution and using compressed air to blow the fluid into and through the substrate, ensuring coating of the cells and also ensuring that there are no or practically no blocked cells.

We have realised that such processes are not very flexible and have a number of other disadvantages. The slurry or solution is recycled, but the absorption characteristics of the substrate or washcoated substrate are such that certain components, *eg* finer particles or certain dissolved platinum group metal salts, deposit preferentially, thus changing the composition of the recycled fluid and accordingly altering some of the characteristics of the subsequently coated catalysts. We have accordingly realised that continuous processes may not provide the best answer for producing catalysts with identical performance and other characteristics. The present invention provides a batch or semi-batch process that offers very significant improvements in producing car catalysts, with advantages in consistency and control of raw materials, as well as offering catalyst design options not previously available for large scale manufacturing. It is believed that the present invention may have particular applicability in the coating of very high cell density substrates which are difficult to coat using conventional technology.

We are aware of some prior proposals which have some of the objectives of the present invention. For example, in USP 5543181, catalyst solution is sprayed into the cells of a honeycomb support through probes which are inserted into the cells. Such a system is mechanically complex and not capable of coping with very high cell density substrates. USP 4931419 discloses a method of soaking one end of a monolithic support in a specified volume of liquid, equal to the pore volume of the support and turning the monolithic support

over to cause the liquid to drain through the support. Such a method still permits losses of valuable precious metal catalysts. USP 5422138 teaches a coating apparatus involving dipping the base of a monolithic support into a coating liquid then blowing excess liquid from the cells. WO 97/48500 describes a further catalyst coating system where a substrate is partially immersed in a coating liquid, a vacuum is applied to draw the liquid up into the cells of the substrate to a distance less than the length of the cells. Such a system is not very flexible and still recycles coating liquid.

A further proposal is disclosed in GB 2,012,616, which discloses apparatus and methods for coating catalyst substrates using a measured charge of slurry which is drawn into and through the substrate. It is clear that the charge of slurry is such that it is in excess of that actually required to coat the substrate. It is not believed that this proposal was ever developed to the stage of commercial utility. We believe that the fact that excess slurry is used, which is recycled for re-use, results in the alteration of composition in time as various components of the slurry deposit preferentially onto the walls of the substrate.

The present invention provides a monolithic support coating apparatus, comprising means for dosing a pre-determined quantity of a liquid component such quantity being such that it is substantially wholly retained within the intended support, liquid component containment means locatable on the top of a support to receive said quantity of liquid component and pressure means capable of withdrawing the liquid component from the containment means into at least a portion of the support.

The invention further provides a method of coating a monolithic support, comprising the steps (a) locating a containment means on top of a support, (b) dosing a pre-determined quantity of a liquid component into said containment means, either in the order (a) then (b) or (b) then (a), and (c) by applying pressure or vacuum, drawing said liquid component into at least a portion of the support, and retaining substantially all of said quantity within the support. The method may, but need not, provide plug flow into the support.

Desirably, no more than 1wt% of the liquid, more preferably no more than 0.5%, especially none of the liquid, is drawn through the substrate and expelled.

The liquid component may be any liquid used to coat a monolithic support, whether or not it contains catalytic components. In general, this will be a slurry of particles, *eg* absorber or a washcoat slurry, or a solution of catalytically active components, although for certain advanced design catalysts, a washcoat slurry may contain catalytically active particles or solutions. The actual composition of the liquid component is not important for the present invention.

Part of the present invention is a liquid component containment means which is located on top of a support to be coated. Whilst the design and function of this will be better appreciated from the specific description hereinafter, it should be understood to comprise at least a wall generally corresponding to the cross-sectional shape of the support. It may also comprise a permeable base closing the walls to form a container. The wall may be manufactured from plastics, including polypropylene or preferably PTFE, metal, especially stainless steel or PTFE-coated stainless steel, or ceramic, and the base may be a perforated or porous metal plate, sintered metal sponge, a woven or non-woven fabric or a synthetic open cell foam. In certain embodiments, the base or part thereof may be moveable in the manner of a guillotine, iris or shutter, or a separate permeable base, for example applied to the face of the support, may be used. Combinations of different materials may be used, for example, the foam is useful to distribute the liquid evenly across the face of the support, and hence ensure even coating. For certain coating components, the rheology may be such that the component does not begin to enter the cells of the support until pressure or vacuum is applied, and hence no permeable base is required to contain the liquid component.

The containment means need not, and in certain preferred embodiments is designed not to, contain and hence locate the liquid component over the entire upper surface area of the support. The containment means may be shaped to blank off areas of the support, so that coating is not carried out in those areas. For example, in a car catalyst or absorber which is mounted in a housing in the exhaust, the support is sealed around its edges to prevent gas

flow by-passing the support. The effect is to seal off a circumferential quantity of cells, so that these cells are not used for catalysis or absorption/desorption and therefore their content of precious metal catalyst or absorber may be considered to be wasted. The present invention offers the possibility of not coating such circumferential cells. It is also well understood that for a variety of reasons, gas flow is concentrated in the central portion of a monolith, and the present invention permits such a central portion to be coated with a different composition and/or different concentration of components. Accordingly, the containment means may be divided internally to separate different liquids for coating, or parts may be blanked off to prevent coating. It is within the present invention to modify the base of the containment means to achieve a desired coating profile or to yield a desired product. For example, the base may have differing permeability to give easier flow, and hence greater coating deposits, in certain regions, or the base may itself act as a profiled containment means, *eg* by machining a honeycomb monolith, so that certain regions contain greater quantities of liquid component which are transferred directly to corresponding parts of the support located below the base.

It will be understood that the containment means is desirably provided with sealing means effective to prevent loss of coating liquid when pressure/vacuum is applied. Such sealing may be achieved by using a deformable permeable base, or by a separate seal. One preferred type of seal is an inflatable seal, which may be inflated and deflated under machine control. An inflatable seal permits the apparatus to cater for variations in substrate diameter or circumference. If all the cells of a honeycomb support, or all the area of any other type of support, require to be coated, it is not possible to seal on the top face of the support and accordingly a suitable seal against the outer side of the support enables the coating liquid to access the whole of the support.

It is possible to conceive of the development of accurate dosing means which together with a gel-like liquid component, deposits the coating component onto a support without requiring containment means. This modification of the present invention may be considered as using the structure of the liquid component itself as the containment means and hence is within the scope of the invention.

The liquid dosing means may be engineered using generally known principles. For example, there are commercially available machines capable of highly accurate dosing by volume or weight of liquids, for example used for filling in the food or paint industry. These machines are capable of handling liquids of many different viscosities and rheologies.

5 We believe that the accuracy of dosing using current technology is  $\pm 0.1\text{ wt}\%$ . This permits a very significant improvement in coating accuracy according to the present invention. It should also be mentioned that the accuracy of the coating process is also dependent upon the accuracy of the liquid (solution or slurry) analysis. However, the invention offers greatly increased opportunities for control of all aspects of coating.

10 It is desirable to combine the dosing means with automatic handling equipment, which may include a rotatable indexed table capable of moving supports past a number of work stations at which the various stages of the method may take place. Robotic handling may be provided to load and unload supports, and it is envisaged that the method may be  
15 used to part-coat the support in the axial direction, then turn the part-coated support and coat the remainder from the other face. It will be appreciated that the basic apparatus is extremely flexible, and can be designed to have easily changeable dosing means and containment means, and a number of different coating functions may be carried out in the same apparatus. Of course, the invention includes essentially manual operation, which may  
20 be appropriate for low volume, low labour cost applications.

In a further embodiment of the present invention, the dosing head and containment means are combined into a unitary structure which may be located on top of the support, and either moved into fluid connection with a source of the coating liquid, or is permanently  
25 connected thereto, possibly using flexible lines to permit movement of the dosing head and/or the support.

The apparatus and method of the invention may provide plug flow of the dispensed quantity of liquid into the support. An important characteristic of the invention is that  
30 substantially all of the liquid is retained within the support, ensuring even distribution in the desired pattern, and ensuring that there is no significant excess liquid requiring recycling.



Any small quantities of liquid which are not retained within the support are captured in the preferred embodiments in the vacuum hood as illustrated hereinafter, thus improving the health and safety environment.

5           Although the invention may operate using air pressure or a combination of air pressure and vacuum to initiate transfer of the liquid from the containment means into the support, we presently prefer to use the application of a vacuum to the bottom of the support, causing normal air pressure to force the liquid into the cells of the support. If necessary, a pulse of air flow may be initiated to clear the cells of the support and prevent blockages. In  
10 more advanced embodiments, the vacuum itself may be non-uniformly applied, either temporally or spatially.

The quantity of liquid component is pre-determined according to the desired coating design and the behaviour of the liquid component to coat the support without excess, by  
15 conventional experimental methods. The liquid is desirably stored in a large volume container which may be stirred and will be replenished from time-to-time. Since the apparatus provides accurately measured volumes and no recycling, the quality or composition of the liquid component remains constant, and losses are reduced.

20           A particular advantage of the invention in the manufacture of catalysts is that usage of precious metal is very well controlled, and it is not so necessary to over-specify metal loadings in order to cope with process variations.

25           After coating, the support may be dried, and fired if required, to fix or transform the coating.

The invention will now be described by way of example only with reference to the accompanying drawings, in which

30           Figure 1 is a schematic cross-section of an apparatus according to the invention,  
Figure 2 is a schematic cross-section of two designs of containment means, and

Figure 3 are schematic cross-sections of different product catalysts produced according to the present invention.

Referring to Figure 1, a liquid dosing head is generally indicated by 1. This may be adapted from a food container filling machine. The dosing head draws pre-determined volumes of liquid from a pre-mixed supply held in a reservoir (not shown). A containment means, 2, consists of an annular wall, 3, having a permeable membrane base, 4. The containment means is locatable on top of a catalyst support unit, 5, which may be an extruded honeycomb monolith. The monolith 5 is located in a depression, 6, in a work table, 7, the depression being closed by an air-permeable base, 8. A vacuum hood, 9, is sealed around the permeable base 8 and is connected to a controlled source of vacuum. The containment means 2 is shown mounted with a further hood, 10, which is optional and may be used to apply pressure to the liquid held in the containment means.

From the figure, it can readily be appreciated that the pre-determined volume of liquid is held above the monolith until vacuum and/or over-pressure is applied, at which time the liquid is drawn into and retained within the cells of the monolith. Plug flow was observed.

Referring to Figure 2, two head designs are illustrated, particularly suitable for relatively low viscosity liquids such as impregnation solutions. In the drawings, the same identification numbers are used as in Figure 1. In Figure 2a, a seal, 11, is shown to contact the upper surface of the monolith, 5. In Figure 2b, this design is particularly adapted for a metal monolith which has an upstanding lip, 12. The base 4 of the containment means consists of a perforated metal plate, 13, combined with a deformable open cell foam disc, 14. It can be seen that when the containment means is brought down onto the lipped monolith, the foam deforms to provide sealing and a suitable distribution of liquid when liquid flow is initiated.

Figure 3 illustrates the different catalyst designs that can be produced according to the present invention. Taking the catalysts as generally cylindrical, different concentrations

and/or different washcoat and/or catalyst formulations and profiles may be achieved as indicated by different letters A, B and C. It will readily be appreciated that the opportunities for catalyst design to meet specific requirements are greatly increased by the present invention.

5

Although the above description has concentrated on coating car catalysts, the invention may, as has been mentioned, coat many other similar products, and absorbers are particularly suitable. Indeed, the invention permits an absorbent coating to be applied to the same monolithic support as a catalyst coating.

10

The skilled person may readily change many of the details described without departing from the inventive concept.

**CLAIMS**

1. A monolithic support coating apparatus, comprising means for dosing a  
5 pre-determined quantity of a liquid component such quantity being such that it is  
substantially wholly retained within the intended support, liquid component containment  
means locatable on the top of a support to receive said quantity of liquid component, and  
pressure means capable of withdrawing the liquid component from the containment means  
into at least a portion of the support.

10 2. Apparatus according to claim 1, wherein the containment means comprises a base  
permeable to the liquid component.

15 3. Apparatus according to claim 2, wherein the base comprises one or more of a  
perforated or porous metal plate, sintered metal sponge, woven or non-woven fabric or a  
synthetic open cell foam.

20 4. Apparatus according to claim 2 or 3, wherein the base or part thereof comprises a  
moveable part.

5. Apparatus according to any one of the preceding claims, wherein the containment  
means is shaped to cause differential coating of parts of the support.

25 6. Apparatus according to any one of the preceding claims, wherein the pressure means  
comprises a source of vacuum acting on the bottom of the support.

7. Apparatus according to claim 6, wherein an air-permeable base is used to support  
the bottom of the support.

30 8. Apparatus according to any one of the preceding claims, comprising sealing means  
for sealing against undesired leakage or coating during withdrawal of liquid into the support.

9. A method of coating a monolithic support, comprising the steps of (a) locating a containment means on top of a support, (b) dosing a pre-determined quantity of a liquid component into said containment means, either in the order (a) then (b) or (b) then (a), and (c) by applying pressure or vacuum, drawing said liquid component into at least a portion of the support, and retaining substantially all of said quantity within the support.

10. A method according to claim 9, wherein vacuum is applied to the bottom of the support, causing air pressure to force the liquid component from the containment means into the support.

11. A method according to claim 9 or 10, used for the coating of catalyst or absorber supports.

12. A method according to claim 11, wherein the liquid component is a washcoat slurry or a solution of a catalyst component.

13. A catalyst comprising a support coated by the method of claim 11 or 12.

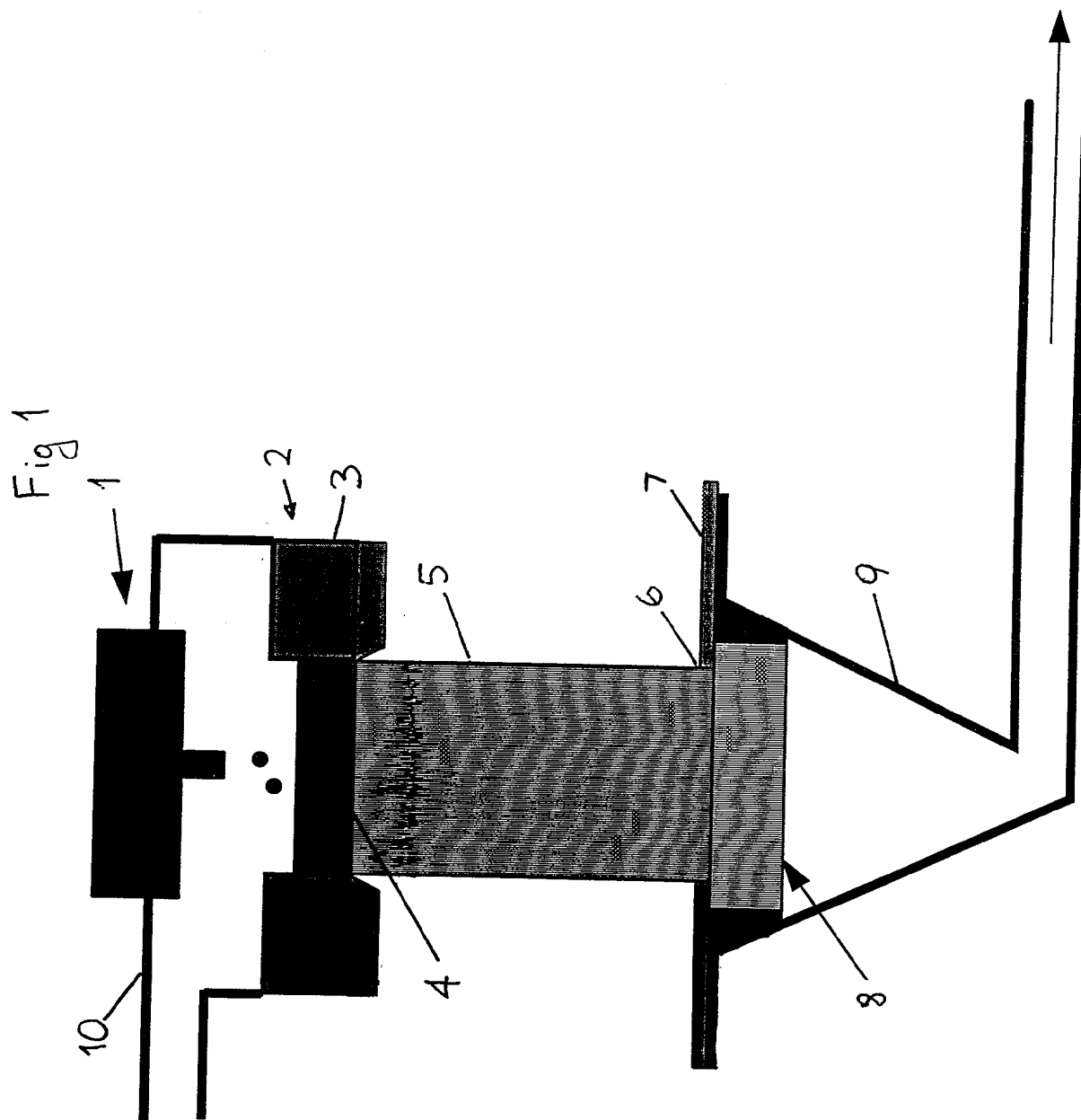


Fig 2

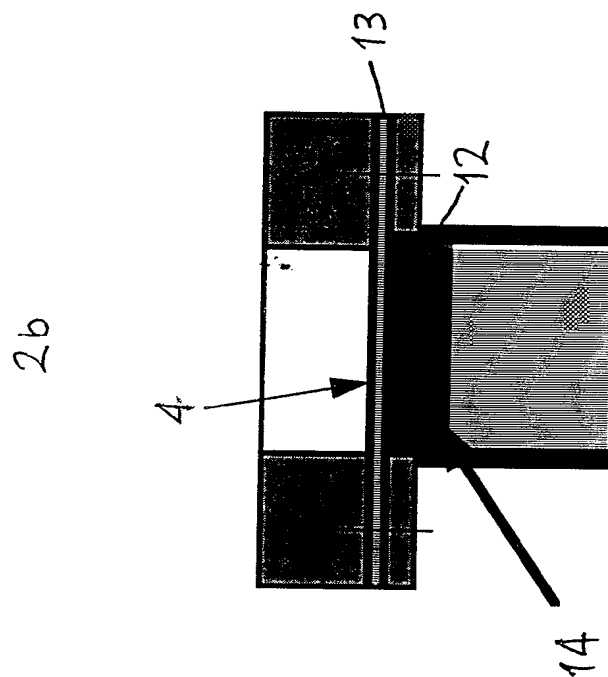
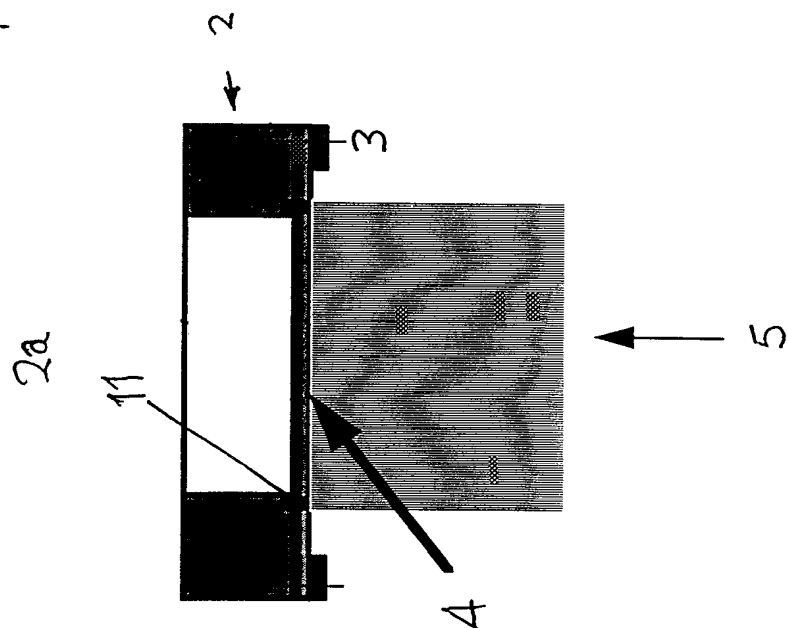
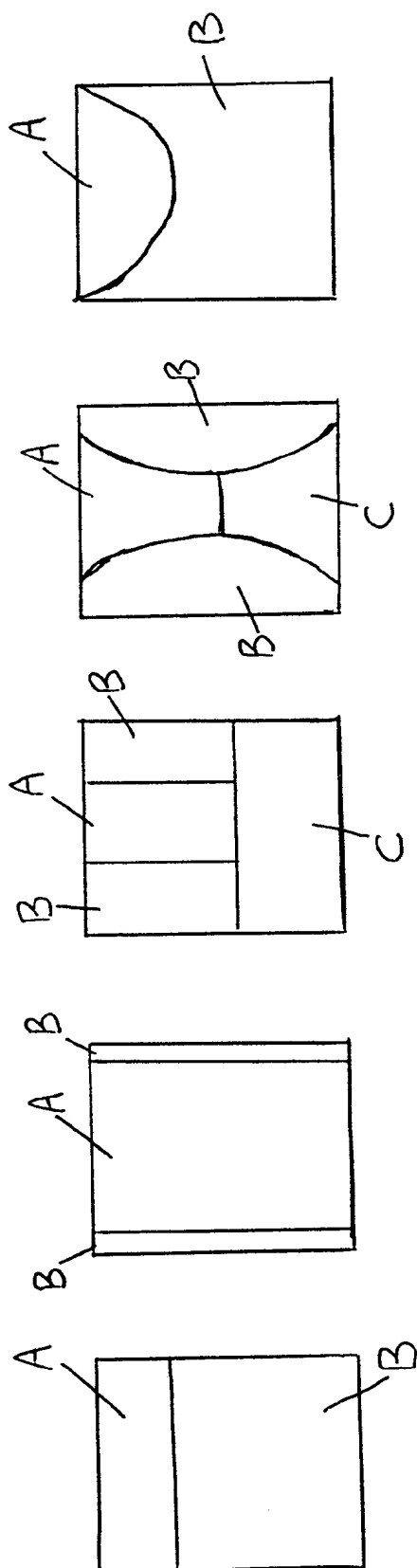


Fig 3





# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/00652

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 B01J37/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J B05C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 012 616 A (GEN MOTORS CORP) 1 August 1979 cited in the application see the whole document	1-3,6-13
X	EP 0 398 128 A (DEGUSSA) 22 November 1990  see the whole document especially page 3, line 20 - line 22	1,2,8,9, 11-13
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 125 (C-283), 30 May 1985 & JP 60 012136 A (TOYOTA JIDOSHA KK), 22 January 1985 see abstract	1,2,5-7, 13
A	-----	9-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

9 June 1999

Date of mailing of the international search report

18/06/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Zuurdeeg, B

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. onal Application No

PCT/GB 99/00652

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2012616 A	01-08-1979	US 4208454 A	17-06-1980
		AU 525782 B	02-12-1982
		AU 4345779 A	26-07-1979
		CA 1109446 A	22-09-1981
		DE 2902073 A	02-08-1979
		JP 54112389 A	03-09-1979
		JP 62028695 B	22-06-1987
		US 4191126 A	04-03-1980
EP 0398128 A	22-11-1990	DE 3915685 C	06-12-1990
		CA 2016537 A	13-11-1990
		JP 3094840 A	19-04-1991
		MX 173626 B	18-03-1994
		RU 2047396 C	10-11-1995
		US 5077093 A	31-12-1991